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Characteristics of carbonaceous aerosols emitted from peatland fire in Riau, Sumatra, Indonesia (2) – Identification of organic compounds –

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Abstract

Smoke emitted from Indonesian peatland fires has caused dense haze and serious air pollution in Southeast Asia such as visibility impairment and adverse health impacts. To mitigate the Indonesian peatland fire aerosol impacts, an effective strategy and international framework based on the latest scientific knowledge needs to be established. Although several attempts have been made, limited data exist regarding the chemical characteristics of peatland fire smoke for the source apportionment. In order to identify the key organic compounds of peatland fire aerosols, we conducted intensive field studies based on ground-based and source-dominated sampling of PM_{2.5} in Riau Province, Sumatra, Indonesia, during the peatland fire seasons in 2012. Levoglucosan was the most abundant compound among the quantified organic compounds at $8.98 \pm 2.28\%$ of the PM_{2.5} mass, followed by palmitic acid at $0.782 \pm 0.163\%$ and mannosan at $0.607 \pm 0.0861\%$. Potassium ion was not appropriate for an indicator of Indonesian peatland fires due to extremely low concentrations associated with smoldering fire at low temperatures. The vanillic/syringic acids ratio was 1.06 ± 0.155 in this study and this may be a useful signature profile for peatland fire emissions. Particulate *n*-alkanes also have potential for markers to identify impact of Indonesian peatland fire source at a receptor site.

Keywords

Peatland fire; PM_{2.5}; Lignin; *n*-alkane; Indonesia

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35 **Highlights**

- 36
- 37 ➤ Organic compounds in PM_{2.5} emitted from peatland fires were characterized.
- 38 ➤ Potassium cannot be used as a source indicator for peatland fires.
- 39 We found some potential source indicators of peatland fire.

40

1. Introduction

Biomass burning (BB) can be defined as an open or quasi-open combustion of a nonfossilized vegetative or organic fuel [Akagi *et al.*, 2011]. BB is the largest source of primary fine carbonaceous aerosols and the second largest source of trace gases in the global atmosphere [Guenther *et al.*, 2006; Andreae and Merlet, 2001; Bond *et al.*, 2011]. Aerosols emitted from BB have direct as well as indirect effects on climate and are a predominant cause of transboundary haze pollution [Tacconi, 2003]. In general, 80% to 90% of smoke aerosols produced by BB are in the PM_{2.5} size range [Reid *et al.*, 2005], indicating the importance of PM_{2.5} as an indicator of BB.

In Indonesia, many hotspots of peatland fires have been detected in the Sumatra and Kalimantan Islands during the dry season. Peatland is a terrestrial wetland ecosystem where organic matter production exceeds its decomposition, resulting in net accumulation [Page *et al.*, 2006]. Smoke emitted from Indonesian peatland fires has caused dense haze and serious air pollution in Southeast Asia such as visibility impairment and adverse health impacts. [Harrison *et al.*, 2009]. Though El Niño–Southern Oscillation (ENSO) events considerably contribute to the occurrence of peatland fires due to biomass dryness under severe drought conditions, pollution from peatland fires is a repeated problem in Indonesia and neighboring countries, even in non-ENSO years [Tacconi, 2003].

To mitigate the Indonesian peatland fire aerosol impacts, an effective strategy and international framework such as ASEAN Agreement on Transboundary Haze Pollution [ASEAN Haze Action

60 Online] based on the latest scientific knowledge needs to be established. Although several
61 attempts have been made, limited data exist regarding the chemical characteristics of peatland fire
62 smoke [Betha *et al.*, 2013; Fujii *et al.*, 2014; See *et al.*, 2007] for source speciation. Recently, we
63 determined the main components of PM_{2.5} in the vicinity of Indonesian peatland fires and showed
64 organic carbon constituted ~70% of the PM_{2.5} mass, indicating organic matter is extremely
65 important [Fujii *et al.*, 2014]. In general, each individual plant species emits a chemical
66 fingerprint of natural and thermally altered organic constituents upon burning, which is source
67 specific and unique in composition [Oros *et al.*, 2006]. See *et al.* (2007) reported polycyclic
68 aromatic hydrocarbons and water soluble organic ions in PM_{2.5} collected in the open field within
69 a 100 m circumference from the boundary of the peatland fires. However, these compounds
70 accounted for only ~1.45 weight% of PM_{2.5}. Therefore, it is necessary to explain the organic
71 compounds in Indonesian peatland fire aerosols in depth and find key source indicators.

72 In this study, we quantitatively characterized major organic compounds of the aerosols derived
73 from Indonesian peatland fires to determine potential source profile and indicators. These data
74 will provide useful information to evaluate the contribution of Indonesian peatland fire aerosols
75 to the air quality in Southeast Asia.

76

2. Materials and methods

2.1. Sampling locations

The sampling was performed in Riau, Sumatra, Indonesia. A detailed description about the sampling sites has been given in our former report [Fujii *et al.*, 2014]. In brief, the sampling site was located at Sepahat Village in Bengkalis Regency, Riau Province, Sumatra, Indonesia. The sampling site was enclosed by peatland and forest, and the rainy season lasts from September to January, with an average rainfall of 809–4078 mm year⁻¹, and the dry season normally lasts from February to August.

2.2. Sample collection and analysis

PM_{2.5} aerosol samples emitted from peatland fires were collected on June 14–16, 2012. Peat soil, fallen trees (hardwoods), oil palm, and bush were mainly burned during this period. Two mini-volume samplers (MiniVolTM TAS, Airmetrics) were utilized to continuously collect PM_{2.5} aerosols on Teflon and quartz fiber filters for 2.5–5.2 h at a flow rate of 5 L min⁻¹. PM_{2.5} aerosols were collected at ~1.5 m above ground level from several peatland fire hotspots on 7 occasions. Wind speeds in the peatland fire samplings ranged from 0.610 to 6.21 m s⁻¹ (average speed: 2.50 m s⁻¹), and aerosols were collected in smoke plumes.

Quartz fiber filters were heat-treated at 900 °C for 4 h before sampling to remove any absorbed

95 organic material. After sampling, Teflon and quartz fiber filters were stored in a refrigerator under
96 4 and -20°C , respectively, until analysis. Each Teflon filter was weighed using a microbalance
97 (ME5-F, Sartorius) with a sensitivity of $\pm 1\text{ }\mu\text{g}$ in a stable environment of $25.7 \pm 0.4\text{ }^{\circ}\text{C}$ (average \pm
98 standard deviation) and $26.0 \pm 0.6\text{ RH}\%$ before and after sampling to determine $\text{PM}_{2.5}$ mass
99 concentrations. After gravimetric analysis, each Teflon filter was analyzed for water-soluble
100 inorganic ions by ion chromatography (HIC-10A, Shimadzu). In this study, only data of
101 potassium ions (K^{+}) is considered for discussion.

102 Solvent-extractable organic compounds obtained from the quartz fiber filters were quantified
103 by gas chromatography/mass spectrometry (GC/MS). Organic compound speciation was
104 accomplished as follows. Aliquots from the quartz fiber filter were spiked with internal standards
105 of methyl β -L-arabinopyranoside, 1,2,3-hexanetriol, (S)-(+)-ketopinic acid, and triacontane- d_{62}
106 before extraction. Each spiked filter was extracted by ultrasonic agitation for $3 \times 20\text{ min}$ periods
107 using 4 mL of a dichloromethane/methanol mixture (3/1, v/v) (dichloromethane: Kanto Chemical,
108 purity $>99.5\%$; methanol: Wako, purity $>99.7\%$). The combined extracts were filtered through a
109 Teflon syringe filter (pore size $0.1\text{ }\mu\text{m}$), dried completely under a nitrogen stream, and
110 redissolved to 2 mL in a dichloromethane/methanol mixture (3/1, v/v). Subsequently, 1 mL of the
111 concentrated extracts were dried completely under a nitrogen stream and used for derivatization
112 as follows. Before GC/MS analysis, trimethylsilyl derivatization was conducted for the extracts

113 with 10 μL of *N,O*-bis-(trimethylsilyl)-trifluoroacetamide with 1% trimethylchlorosilane and 45
114 μL of pyridine for 3 h at 70 $^{\circ}\text{C}$, and then ~ 9 μg of tetracosane-*d*₅₀ dissolved in 45 μL of
115 dichloromethane was added as a syringe spike (second internal standard).

116 The derivatized samples were analyzed on a Shimadzu GC/MS system (GCMS-QP2010-Plus,
117 Shimadzu) equipped with a 30 m HP-5MS column (0.25 μm film thickness, 0.25 mm ID). The
118 carrier gas was helium (purity 99.9995%) at a pressure of 59.4 kPa (36.6 cm s^{-1} at 65 $^{\circ}\text{C}$). The
119 GC oven temperature program was as follows: isothermal at 65 $^{\circ}\text{C}$ for 5 min, 65 $^{\circ}\text{C}$ to 300 $^{\circ}\text{C}$ at
120 10 $^{\circ}\text{C min}^{-1}$, and then 300 $^{\circ}\text{C}$ for 20 min. The injection port and transfer line were maintained at
121 300 $^{\circ}\text{C}$. The data for quantitative analysis were acquired in the electron impact mode (70 eV).
122 The mass spectrometer was operated under selected ion monitoring mode, and the monitored ions
123 for quantification are shown in Table 1. Regarding internal standards, the monitored ions of
124 methyl β -L-arabinopyranoside, 1,2,3-hexanetriol, (*S*)-(+)-ketopinic acid, triacontane-*d*₆₂, and
125 tetracosane-*d*₅₀ were 217, 145, 75, 66, and 66 m/z , respectively. The recovery ratios of known
126 amounts of the standards on quartz fiber filters are presented in Table 2. In addition,
127 solvent-extractable organic compounds as targets on field blank filters were analyzed, which
128 showed no contamination.

129

3. Results and discussion

PM_{2.5} mass concentrations and fractions of organic compounds in PM_{2.5} emitted from peatland fires are shown in Table 3. The PM_{2.5} mass concentration was $7130 \pm 3630 \mu\text{g m}^{-3}$, and quantified organic compounds accounted for $14.4 \pm 2.55\%$ of the PM_{2.5} mass. Though particulate K⁺ has been suggested as a tracer for BB [Chuang *et al.*, 2013], it was only $0.0423 \pm 0.0400\%$ of the PM_{2.5} mass in this study. Levoglucosan was the most abundant compound among the quantified organic compounds at $8.98 \pm 2.28\%$ of the PM_{2.5} mass, followed by palmitic acid at $0.782 \pm 0.163\%$ and mannosan at $0.607 \pm 0.0861\%$.

3.1. Cellulose pyrolysis products

Levoglucosan mainly derived from pyrolysis of cellulose is widely accepted as a major organic component in fine smoke aerosols from BB. Mannosan and galactosan are minor constituents compared to levoglucosan and are derived from the pyrolysis of hemicellulose. These compounds cannot be formed by hydrolysis or by the microbial alteration of carbohydrate and are specific to burning [Simoneit *et al.*, 1999].

The K⁺/levoglucosan ratio can be used as an indicator to roughly estimate the combustion state such as flaming or smoldering combustion of BB [Gao *et al.*, 2003; Pio *et al.*, 2008; Chaung *et al.*, 2013]. This is because more K⁺ remains in the aerosol phase compared with levoglucosan when the combustion temperature is higher [Chuang *et al.*, 2013]. For flaming and smoldering

savannah forest fires, the ratios were 33.3 and 0.2–0.6, respectively [Gao *et al.*, 2003]. In this study, the K^+ /levoglucosan ratio was 0.00537 ± 0.00562 and extremely lower than the ratios reported anywhere else [e.g., Gao *et al.*, 2003; Sullivan *et al.*, 2008]. This indicates the Indonesian peatland fires studied were predominantly smoldering at even lower temperature than the smoldering combustions of other BBs in previous studies. An extremely low K^+ fraction ($0.0423 \pm 0.0400\%$ of $PM_{2.5}$ mass) also supports that conclusion. Thus, unlike many other BB sources, K^+ derived from the Indonesian peatland fires should not be used as a source indicator. Other specific indicators are badly needed.

3.2. Lignin pyrolysis products

Lignin is one of the major components of biomass (20–35 wt% of dry matter), and is known to be an aromatic polymer consisting of phenylpropane units linked through various ether and C–C types of linkages. Its aromatic structures vary depending on the species; softwood lignins contain guaiacyl (G) types exclusively, whereas hardwood lignins include both G and syringyl (S) types, and herbaceous plants include G, S, and *p*-hydroxyphenyl types. Thus, the compositions of these aromatic nuclei in the lignin pyrolysis products from BB would be useful for identifying the biomass type. In fact, Simoneit *et al.* (1993) reported that lignin pyrolysis products in BB aerosols have the potential to provide a unique source signature or profile.

In this study, various lignin G- and S-unit-originated compounds had higher yields. Vanillin

(V), coniferyl aldehyde, vanillic acid (VA), and homovanillic acid are derived from the G units, whereas syringaldehyde (S), syringic acid (SA), and homosyringic acid are derived from the S units. The detection of both G- and S-derived compounds is explicable that the vegetation in the Indonesian peatland mainly consists of hardwood and herbaceous species. There was no detection of dehydroabietic acid as a resin pyrolysis product, as frequently reported for SWB (Softwoods burning) [Simoneit, 1977; Lin *et al.*, 2010], which is also consistent with the vegetation.

VA and SA derived from lignin pyrolysis were abundant organic compounds in our samples (VA: 5.63 ± 1.45 , SA: 5.37 ± 1.33 mg g⁻¹ PM_{2.5}) comparable to palmitic acid (7.82 ± 1.63 mg g⁻¹ PM_{2.5}) and mannosan (6.07 ± 0.861 mg g⁻¹ PM_{2.5}) as shown in Table 3. These two compounds have been detected during the haze episodes in Malaysia [Abas *et al.*, 2004] and Singapore [He *et al.*, 2010], suggesting that the haze arose from Indonesian peatland fires. Therefore, these two compounds may travel long distances (~300 km) as smoke from Indonesian peatlands to Malaysia. Since the relative content of G and S units in lignin are different depending on the biomass type, as discussed above, the VA/SA mass ratios from BB would also vary. Consequently, the mass ratio of VA/SA is expected to be used as an indicator for BB source discrimination. The VA/SA mass ratio in the peatland fire was 1.06 ± 0.155 . For comparison with other BB samples, VA/SA ratios reported for various source samples are presented in Fig. 1, which shows differences in VA/SA ratios between peatland fire and other emission sources in tropical zone.

188 Thus, this ratio has the potential for the source discrimination of peatland fire in tropical zone.
189 Comparison of the VA/SA ratio with those of the sources in Southern United States and
190 California (Fig. 1) may also indicate VA/SA ratio can be a potential indicator for source
191 discrimination. However, there are few reports regarding SA and VA at sources [Fine *et al.*, 2002;
192 Nolte *et al.*, 2001; Oros *et al.*, 2006; Simoneit *et al.*, 1993; 1999]. Further accumulation of these
193 data at several sources is required to enhance the usefulness of SA/VA ratio as a source indicator.

194 The relationships between the aldehydes (V or S) and carboxylic acid (VA or SA) contents in
195 PM_{2.5} collected at peatland fire sources are shown in Fig. 2. Linear regressions through the origin
196 in Fig. 2 were assumed because V/VA and S/SA ratios must be zero when V and S are equal to
197 zero, respectively. Interestingly, the results show fairly good linear relationships, with slopes of
198 0.122 ± 0.0224 (V/VA, coefficient of determination: $R^2 = 0.887$) and 0.446 ± 0.0905 (S/SA, $R^2 =$
199 0.955). Note that the V/VA and S/SA ratios were fairly constant independent of the sampling sites
200 of the peatland fires. Due to the nature of aldehydes, V and S are expected to be more susceptible
201 to photochemical and/or chemical oxidation than VA or SA during their movement away from the
202 peatland fire. Net *et al.* (2011) reported the heterogeneous reactions of ozone with V, S, VA and
203 SA, in presence and absence of simulated solar light. They showed that VA and SA were the main
204 oxidation products of V and S, respectively, and no reaction product from VA and SA was
205 detected during the ozonolysis of VA and SA under 6 ppm ozone concentration. Since conversion

206 rates of V to VA and S to SA are not necessarily identical, the VA/SA ratios may be changed
207 during transportation of peatland fire aerosols. Therefore, we estimated possible variations of this
208 ratio derived from peatland fires under several conditions by oxidation in the atmosphere as
209 follows: (1) all V is completely converted to VA, (2) all S is completely converted to SA, (3) all V
210 and S are completely converted to VA and SA, respectively, (4) present condition (this study). It
211 is shown that at most, variation of VA/SA ratios ranged from -32.5 to 14.2% (Table 4). These
212 possible variations will not largely affect source discrimination for peatland fires.

213

214 3.3. *n*-alkanes

215

216 Particulate *n*-alkanes originate from both biogenic and anthropogenic sources. Anthropogenic
217 sources of *n*-alkanes include incomplete fossil fuel combustion, lubricant oils, and biomass
218 burning, while wind erosion of leaf epicuticular waxes, direct suspension of pollen, vegetation
219 debris, and microbial degradation are major natural sources of particulate *n*-alkanes [Ladji *et al.*,
220 2014; Simoneit, 1989; Rogge *et al.*, 1993a, b; Kavouras *et al.*, 2002]. In this study, we mainly
221 focus on *n*-alkanes more than C₁₉ (nonadecane) since *n*-alkanes less than C₂₀ (icosane) may
222 result in some volatilization from the filter in tropical zone [Abas *et al.*, 2004].

223 Total particulate *n*-alkanes (C₂₀–C₃₃) mass were abundant at 2.15 ± 0.490 weight% of PM_{2.5}
224 mass in this study. Table 3 shows the mass fraction of individual particulate *n*-alkanes in PM_{2.5}.
225 The carbon number maximum concentration in *n*-alkanes was C₂₇, indicating that peatland fire

source was categorized as biogenic sources (higher plant wax) [Abas *et al.*, 2004].

For comparison of our peatland fire samples with other emission sources, mass fraction of particulate total *n*-alkanes (C_{20–33}) in PM for various source samples are presented in Fig. 3. Particulate total *n*-alkanes from noncatalyst-equipped automobiles, catalyst-equipped automobiles, heavy-duty diesel trucks, tire wear, road dust, and brake lining sources were in the PM_{2.0} size range [Rogge *et al.*, 1993a, b]. Particulate total *n*-alkanes from pine wood with green needles burning and savanna grass burning sources were in the PM_{3.5–0.05} range [Iinuma *et al.*, 2007]. Particulate total *n*-alkanes from meat cooking source were in the PM_{1.8} range [Schauer *et al.*, 1999]. Figure 3 shows significant differences in the fraction of total *n*-alkanes (C_{20–33}) in PM between the peatland fire and other emission sources. In particular, the fraction of peatland fire source was much higher than those from tire wear, road dust, brake lining, pine wood with green needles burning, savanna grass burning, and meat cooking.

Figure 4 illustrates the comparison of molecular distributions of particulate *n*-alkanes obtained from our peatland fire samples and vehicle-related emission sources which show high abundance of particulate *n*-alkanes in PM (see Fig. 3). The distribution of particulate *n*-alkanes in PM emitted from peatland fires obviously differs from those of other emissions. Particularly, C₂₇, C₂₈, and C₂₉ mass fractions in particulate total *n*-alkanes (C_{20–33}) in this study were 4.57–26.6 times higher than those from other emissions as shown in Fig. 4. Thus, if a receptor site is affected by

244 Indonesian peatland fire source, C_{27} , C_{28} , and C_{29} mass concentrations and fractions in
245 particulate total n -alkanes (C_{20-33}) would be increased.

246 Abas et al. (2004) reported particulate n -alkanes (C_{15-36}) concentrations in PM during the haze
247 episodes in Kuala Lumpur, Malaysia. At that time, particulate total n -alkanes (C_{15-36})
248 concentrations ranging from 410 to 1009 ng m^{-3} during the haze episodes were much higher than
249 that (C_{16-41}) at the non-haze day of 26 ng m^{-3} , as well as levoglucosan [Abas *et al.*, 1996, 2004].
250 The four molecular distributions of particulate n -alkanes (C_{20-33}) during the haze episodes in
251 Malaysia were reconstructed in Fig. 5 according to their paper [Abas *et al.*, 2004], and compared
252 with that of our peatland fire samples. DUMG and DSP samples were collected during the day
253 time, and NUMG and NSP samples were collected during the night time. Roughly, the molecular
254 distributions of particulate n -alkanes during the haze episodes in Malaysia were comparable to
255 that of our peatland fire samples. Increase in total concentrations and molecular distributions of
256 particulate n -alkanes during the haze episodes are considered to be caused by Indonesian peatland
257 fires. Therefore, particulate n -alkanes can serve as potential markers to identify impact of
258 Indonesian peatland fire source at a receptor site like Malaysia.

259

4. Conclusion

In order to identify the key organic compounds of peatland fire aerosols, we conducted intensive field studies based on ground-based and source-dominated sampling of PM_{2.5} in Riau Province, Sumatra, Indonesia, during the peatland fire seasons in 2012. Levoglucosan was the most abundant compound among the quantified organic compounds at $8.98 \pm 2.28\%$ of the PM_{2.5} mass, followed by palmitic acid at $0.782 \pm 0.163\%$ and mannosan at $0.607 \pm 0.0861\%$. K⁺ was not appropriate for an indicator of Indonesian peatland fires due to extremely low concentrations associated with smoldering fire at low temperatures. In terms of lignin pyrolysis products, V/VA and S/SA ratios were fairly constant independent of the sampling sites of the peatland fires. The VA/SA ratio was 1.06 ± 0.155 in this study and this may be a useful signature profile for peatland fire emissions after allowing for the uncertainty of the conversion rates of aldehydes (V, S) to acids (VA, SA). Particulate *n*-alkanes also have potential for markers to identify the impact of Indonesian peatland fire source at a receptor site.

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REFERENCES

- Abas, M.R. and B.R.T. Simoneit (1996), Composition of extractable organic matter of air particles from Malaysia: Initial study. *Atmos. Environ.*, 30(15), 2779–2793, doi:10.1016/1352-2310(95)00336-3.
- Abas, M.R., D.R. Oros, and B.R.T. Simoneit (2004), Biomass burning as the main source of organic aerosol particulate matter in Malaysia during haze episodes. *Chemosphere*, 55(8), 1089–1095, doi:10.1016/j.chemosphere.2004.02.002.
- Akagi, S.K., R.J. Yokelson, C. Wiedinmyer, M.J. Alvarado, J.S. Reid, T. Karl, J.D. Crounse, and P.O. Wennberg (2011), Emission factors for open and domestic biomass burning for use in atmospheric models. *Atmos. Chem. Phys.*, 11(9), 4039–4072, doi:10.5194/acp-11-4039-2011.
- Andreae, M.O., and P. Merlet (2001), Emission of trace gases and aerosols from biomass burning. *Global Biogeochem. Cy.*, 15(4), 955–966, doi:10.1029/2000GB001382.
- ASEAN Haze Action Online. [online] [Accessed 11 December 2013]. Available: <http://haze.asean.org>.
- Betha, R., M. Pradani, P. Lestari, U.M. Joshi, J.S. Reid, and R. Balasubramanian (2013), Chemical speciation of trace metals emitted from Indonesian peat fires for health risk assessment. *Atmos. Res.*, 122, 571–578, doi:10.1016/j.atmosres.2012.05.024.
- Bond, T.C., D.G. Streets, K.F. Yarber, S.M. Nelson, J.-H., Woo, and Z. Klimont (2004), A

- 299 technology-based global inventory of black and organic carbon emissions from combustion. *J.*
- 300 *Geophys. Res.* 2004, 109, D14203, doi:10.1029/2003JD003697.
- 301 Chuang, M.T., C.C.K. Chou, K. Sopajaree, N.H. Lin, J.L. Wang, G.R. Sheu, Y.J. Chang, and C.T.
- 302 Lee (2013), Characterization of aerosol chemical properties from near-source biomass burning
- 303 in the northern Indochina during 7-SEAS/Dongsha experiment. *Atmos. Environ.*, 78, 72–81,
- 304 doi:10.1016/j.atmosenv.2012.06.056.
- 305 Fine, P.M., G.R. Cass, and B.R.T. Simoneit (2002), Chemical characterization of fine particle
- 306 emissions from the fireplace combustion of woods grown in the Southern United States.
- 307 *Environ. Sci. Technol.*, 36(7), 1442–1451, doi:10.1021/es0108988.
- 308 Fujii, Y., W. Iriana, M. Oda, A. Puriwigati, S. Tohno, P. Lestari, A. Mizohata, and H.S. Huboyo
- 309 (2014), Characteristics of carbonaceous aerosols emitted from peatland fire in Riau, Sumatra,
- 310 Indonesia. *Atmos. Environ.*, 87, 164–169, doi:10.1016/j.atmosenv.2014.01.037.
- 311 Gao, S., D.A. Hegg, P.V. Hobbs, T.W. Kirchstetter, B.I. Magi, and M. Sadilek (2003),
- 312 Water-soluble organic components in aerosols associated with savanna fires in southern Africa:
- 313 identification, evolution, and distribution. *J. Geophys. Res.*, 108, D13, 8491,
- 314 doi:10.1029/2002JD002324.
- 315 Guenther, A., T. Karl, P. Harley, C. Wiedinmyer, P.I. Palmer, and C. Geron (2006), Estimates of
- 316 global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and

- 317 Aerosols from Nature). *Atmos. Chem. Phys.*, 6(11), 3181–3210, doi:10.5194/acp-6-3181-2006.
- 318 Harrison, M.E., S.E. Page, and S.H. Limin (2009), The global impact of Indonesian forest fires.
- 319 *Biologist*, 56(3), 156–163.
- 320 He, J., B. Zielinska, and R. Balasubramanian (2010), Composition of semi-volatile organic
- 321 compounds in the urban atmosphere of Singapore: influence of biomass burning. *Atmos. Chem.*
- 322 *Phys.*, 10(23), 11401–11413.
- 323 Hennigan, C.J., A.P. Sullivan, J.L. Collett Jr., and A.L. Robinson (2010), Levoglucosan stability
- 324 in biomass particles exposed to hydroxyl radicals. *Geophys. Res. Lett.*, 37, L09806,
- 325 doi:10.1029/2010GL043088.
- 326 Iinuma, Y., E. Brüggemann, T. Gnauk, K. Müller, M.O. Andreae, G. Helas, R. Parmar, and
- 327 H.Herrmann (2007), Source characterization of biomass burning particles: The combustion of
- 328 selected European conifers, African hardwood, savanna grass, and German and Indonesian peat.
- 329 *J. Geophys. Res.*, 112, D08209, doi:10.1029/2006JD007120.
- 330 Kavouras, I.G. and E.G. Stephanou (2002), Particle size distribution of organic primary and
- 331 secondary aerosol constituents in urban, background marine, and forest atmosphere. *J.*
- 332 *Geophys. Res.*, 107, doi:10.1029/2000JD000278.
- 333 Ladji, R., N. Yasaa, C. Balducci, and A. Cecinato (2014), Particle size distribution of *n*-alkanes
- 334 and polycyclic aromatic hydrocarbons (PAHs) in urban and industrial aerosol of Algiers,

- 335 Algeria. *Environ. Sci. Pollut. Res.*, 21(3), 1819–1832, doi:10.1007/s11356-013-2074-2.
- 336 Lin, L., M.L. Lee, and D.J. Eatough (2010), Review of recent advances in detection of organic
- 337 markers in fine particulate matter and their use for source. *J. Air & Waste Manage. Assoc.*,
- 338 60(1), 3–25, doi:10.3155/1047-3289.60.1.3.
- 339 Net, S., E.G. Alvarez, S. Gligorovski, and H. Wortham (2011), Heterogeneous reactions of ozone
- 340 with methoxyphenols, in presence and absence of light. *Atmos. Environ.*, 45(18), 3007–3014,
- 341 doi:10.1016/j.atmosenv.2011.03.026.
- 342 Nolte, C.G., J.J. Schauer, G.R. Cass, and B.R.T. Simoneit (2001), Highly polar organic
- 343 compounds present in wood smoke and in the ambient atmosphere. *Environ. Sci. Technol.*,
- 344 35(10), 1912–1919, doi:10.1021/es001420r.
- 345 Oros, D.R., M.R.B. Abas, N.Y.M.J. Omar, N.A. Rahman, and B.R.T. Simoneit (2006),
- 346 Identification and emission factors of molecular tracers in organic aerosols from biomass
- 347 burning: Part 3. Grasses. *Appl. Geochem.*, 21(6), 919–940,
- 348 doi:10.1016/j.apgeochem.2006.01.008.
- 349 Page, S.E., J.O. Rieley, and R. Wüst (2006), Chapter 7 Lowland tropical peatlands of Southeast
- 350 Asia. In: Martini, I.P., Martinez Cortizas, A., Chesworth, W. (Eds.), *Developments in Earth*
- 351 *Surface Processes*, Elsevier, Vol. 9, *Peatlands: Evolution and Records of Environmental and*
- 352 *Climate Changes*, pp. 145–172.

- 353 Pio, C.A., M. Legrand, C.A. Alves, T. Oliveira, J. Afonso, A. Caseiro, H. Puxbaum, A.
- 354 Sanchez-Ochoa, and A. Gelencser (2008), Chemical composition of atmospheric aerosols
- 355 during the 2003 summer intense forest fire period. *Atmos. Environ.*, 42(32), 7530–7543.
- 356 Reid, J.S., R. Koppmann, T.F. Eck, and D.P. Eleuterio (2005), A review of biomass burning
- 357 emissions part II: intensive physical properties of biomass burning particles. *Atmos. Chem.*
- 358 *Phys.*, 5(3), 799–825, doi:10.5194/acp-5-799-2005.
- 359 Rogge, W.F., L.M. Hildemann, M.A. Mazurek, G.R. Cass, and B.R.T. Simoneit (1993a), Sources
- 360 of fine organic aerosol. 2. Noncatalyst and catalyst-equipped automobiles and heavy-duty
- 361 diesel trucks. *Environ. Sci. Technol.*, 27(4), 636–651, doi:10.1021/es00041a007.
- 362 Rogge, W.F., L.M. Hildemann, M.A. Mazurek, G.R. Cass, and B.R.T. Simoneit (1993b), Sources
- 363 of fine organic aerosol. 3. Road dust, tire debris, and organometallic brake lining dust: Roads
- 364 as sources and sinks. *Environ. Sci. Technol.*, 27(9), 1892–1904, doi:10.1021/es00046a019.
- 365 Schauer, J.J., M.J. Kleeman, G.R. Cass, and B.R.T. Simoneit (1999), Measurement of emissions
- 366 from air pollution sources. 1. C₁ through C₂₉ organic compounds from meat charbroiling.
- 367 *Environ. Sci. Technol.*, 33(10), 1566–1577, doi:10.1021/es980076j.
- 368 See, S.W., R. Balasubramanian, E. Rianawati, S. Karthikeyan, and D.G. Streets (2007),
- 369 Characterization and Source Apportionment of Particulate Matter $\leq 2.5 \mu\text{m}$ in Sumatra,
- 370 Indonesia, during a Recent Peat Fire Episode. *Environ. Sci. Technol.*, 41(10), 3488–3494,

371 doi:10.1021/es061943k.

372 Simoneit, B.R.T. (1977), Diterpenoid compounds and other lipids in deep-sea sediments and their
373 geochemical significance. *Geochim. Cosmochim. Acta*, 41(4), 463–476,
374 doi:10.1016/0016-7037(77)90285-X.

375 Simoneit, B.R.T. (1989), Organic matter of the troposphere V. Application of molecular marker
376 analysis to biogenic emissions into the troposphere for source reconciliations. *J. Atmos. Chem.*,
377 8(3), 251–275, doi:10.1007/BF00051497.

378 Simoneit, B.R.T., J.J. Schauer, C.G. Nolte, D.R. Oros, V.O. Elias, M.P. Fraser, W.F. Rogge, and
379 G.R. Cass (1999), Levoglucosan, a tracer for cellulose in biomass burning and atmospheric
380 particles. *Atmos. Environ.* 1999, 33(2), 173–182, doi:10.1016/S1352-2310(98)00145-9.

381 Simoneit, B.R.T., W.F. Rogge, M.A. Mazurek, L.J. Standley, L.M. Hildemann, and G.R. Cass
382 (1993), Lignin pyrolysis products, lignans, and resin acids as specific tracers of plant classes in
383 emissions from biomass combustion. *Environ. Sci. Technol.*, 27(12), 2533–2541,
384 doi:10.1021/es00048a034.

385 Sullivan, A.P., A.S. Holden, L.A. Patterson, G.R. McMeeking, S.M. Kreidenweis, W.C. Malm,
386 W.M. Hao, C.E. Wold, and J.L. Collett Jr. (2008), A method for smoke marker measurements
387 and its potential application for determining the contribution of biomass burning from wildfires
388 and prescribed fires to ambient PM_{2.5} organic carbon. *J. Geophys. Res.*, 113, D22302,

389 doi:10.1029/2008JD010216.

390 Tacconi, L. (2003), Fires in Indonesia: Causes, Costs and Policy Implications. CIFOR Occasional

391 Paper 38.

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Table Captions

394 Table 1. Analytes, internal standards employed for GC/MS.

395 Table 2. Recovery ratios of target and internal standards.

396 Table 3. Bulk chemical compositions of PM_{2.5} emitted from peatland fires (average \pm standard

397 deviation).

398 Table 4. Possible variations of VA/SA mass ratios derived from peatland fires under several

399 conditions by oxidation in the atmosphere.

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Analyte	m/z used for quantification	Internal Standard
levoglucosan	204	methyl β -L-arabinopyranoside
mannosan	204	methyl β -L-arabinopyranoside
galactosan	204	methyl β -L-arabinopyranoside
vanillin	194	1,2,3-hexanetriol
syringaldehyde	239	1,2,3-hexanetriol
coniferylaldehyde	220	methyl β -L-arabinopyranoside
<i>p</i> -hydroxybenzoic acid	267	methyl β -L-arabinopyranoside
vanillic acid	297	(<i>S</i>)-(+)-ketopinic acid
syringic acid	253	(<i>S</i>)-(+)-ketopinic acid
homovanillic acid	326	methyl β -L-arabinopyranoside
homosyringic acid	239	methyl β -L-arabinopyranoside
palmitic acid	117	methyl β -L-arabinopyranoside
<i>n</i> -alkanes (C _{20–33})	57	triacontane- <i>d</i> ₆₂

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Table 1.

Compounds	Addition [μg]	Recovery ratio [%]	Recoveries of Target/IS [-]
levoglucosan	82.0	94.0±7.58	1.04±0.0461
mannosan	25.5	92.9±9.01	1.03±0.0410
galactosan	9.95	89.0±8.45	0.984±0.0239
vanillin	2.25	86.2±12.2	0.978±0.0832
syringaldehyde	8.70	97.9±13.9	1.11±0.0939
coniferylaldehyde	1.70	101±24.7	1.12±0.205
<i>p</i> -hydroxybenzoic acid	11.8	85.1±6.58	0.943±0.0556
vanillic acid	15.7	84.5±7.14	1.01±0.0757
syringic acid	18.3	92.6±9.93	1.10±0.0964
homovanillic acid	1.00	92.0±13.1	1.02±0.0647
homosyringic acid	1.01	105±14.8	1.17±0.0921
palmitic acid	18.2	98.9±11.3	1.10±0.152
icosane	5.00	85.3±8.13	1.26±0.231
heneicosane	5.00	85.9±8.42	1.27±0.238
docosane	5.00	86.3±9.48	1.27±0.235
tricosane	5.00	85.6±10.9	1.26±0.226
tetracosane	5.00	84.0±12.3	1.23±0.220
pantacosane	5.00	81.9±14.0	1.20±0.215
hexacosane	5.00	80.9±15.4	1.18±0.215
heptacosane	5.00	79.4±16.7	1.16±0.209
octacosane	5.00	77.7±17.8	1.13±0.201
nonacosane	5.00	75.4±18.8	1.09±0.193
triacontane	5.00	72.3±18.9	1.04±0.182
hentriacontane	5.00	69.2±20.4	0.990±0.180
dotriacontane	5.00	66.1±21.4	0.939±0.181
tritriacontane	5.00	62.7±22.6	0.884±0.194
methyl β-L-arabinopyranoside	8.32	90.6±10.1	-
1,2,3-hexanetriol	4.34	88.2±10.1	-
(<i>S</i>)-(+)-ketopinic acid	4.92	84.1±8.30	-
triacontane- <i>d</i> ₆₂	8.40	70.3±16.6	-

Table 2.

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Organic compounds	[mg g ⁻¹ PM _{2.5}]
levoglucosan	89.8±22.8
mannosan	6.07±0.861
galactosan	2.01±0.256
vanillin	0.665±0.124
syringaldehyde	2.30±0.452
coniferylaldehyde	0.329±0.0916
<i>p</i> -hydroxybenzoic acid	1.72±0.346
vanillic acid	5.63±1.45
syringic acid	5.37±1.53
homovanillic acid	0.435±0.0974
homosyringic acid	0.259±0.0702
palmitic acid	7.82±1.63
icosane	0.527±0.339
heneicosane	0.913±0.440
docosane	1.53±0.545
tricosane	1.70±0.473
tetracosane	1.70±0.444
pantacosane	2.62±0.572
hexacosane	1.42±0.399
heptacosane	2.89±0.562
octacosane	2.10±0.297
nonacosane	1.78±0.352
triacontane	0.968±0.180
hentriacontane	1.84±0.368
dotriacontane	0.631±0.112
tritriacontane	0.874±0.152

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Table 3.

<i>Condition by oxidation</i>	<i>VA/SA mass ratio</i>
(1) All V conversion to VA	1.21±0.173
(2) All S conversion to SA	0.715±0.0856
(3) All V and S conversion to VA and SA, respectively	0.811±0.0921
(4) No S and V conversion to VA and SA, respectively	1.06±0.155

Table 4.

Figure Captions

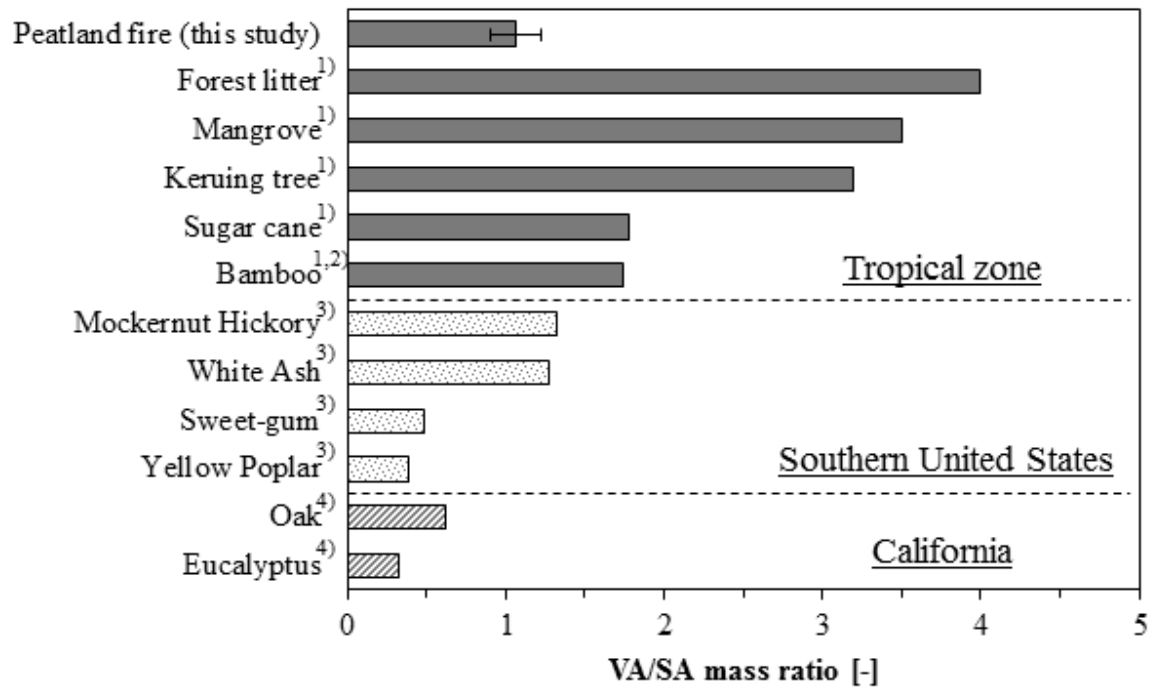
Fig. 1. Comparison of VA/SA mass ratios of PM_{2.5} obtained from peatland fire and other burning sources. Error bar in this study indicates standard deviations.

Fig. 2. Concentrations of G vs. S units derived from lignin pyrolysis in PM_{2.5} emitted from Indonesian peatland fires (R^2 : coefficient of determination).

Fig. 3. Comparison of mass fraction of particulate total *n*-alkanes (C_{20–33}) in PM obtained from peatland fire and other burning sources.

Fig. 4. Comparison of molecular distributions of particulate *n*-alkanes obtained from peatland fire and vehicle-related emission sources.

Fig. 5. Comparison of molecular distributions of particulate *n*-alkanes obtained from our peatland fire samples and four samples during haze episodes in Malaysia.



1) data from Simoneit *et al.*, 1999, 2) data from Oros *et al.*, 2006, 3) data from Fine *et al.*, 2002,
4) data from Nolte *et al.*, 2001.

Fig. 1.

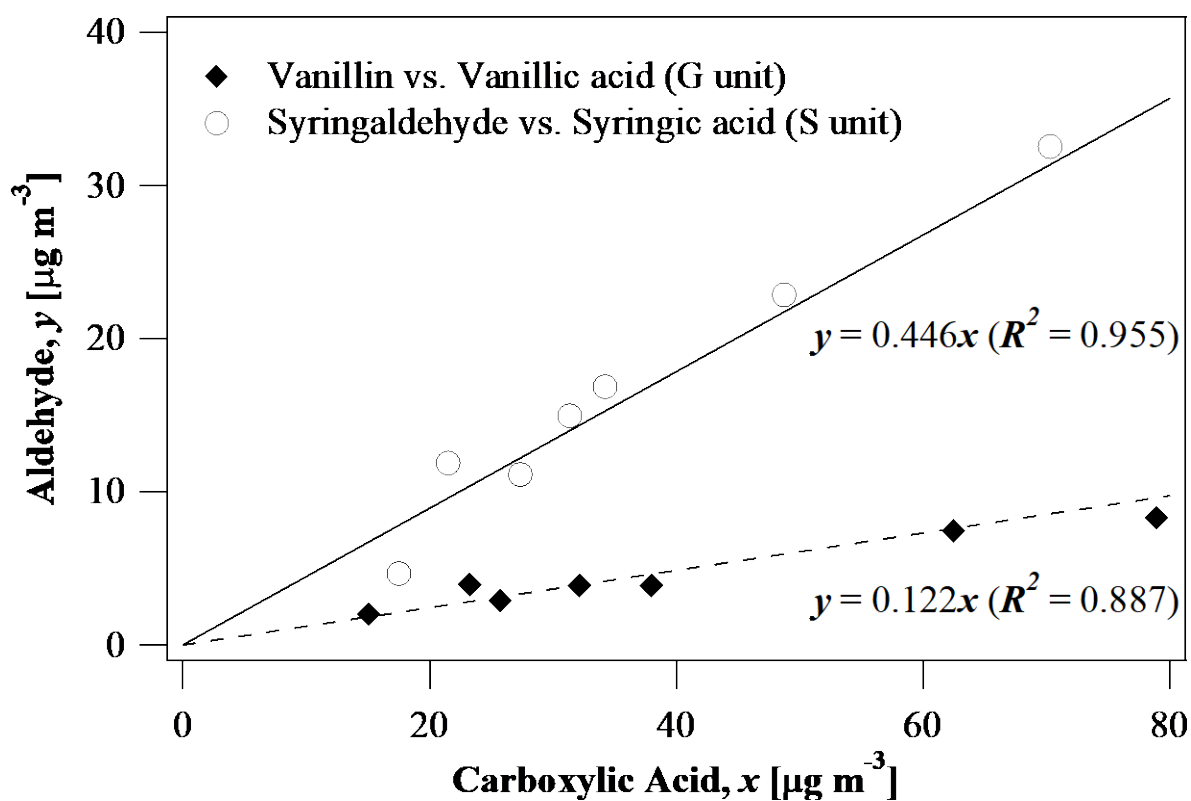
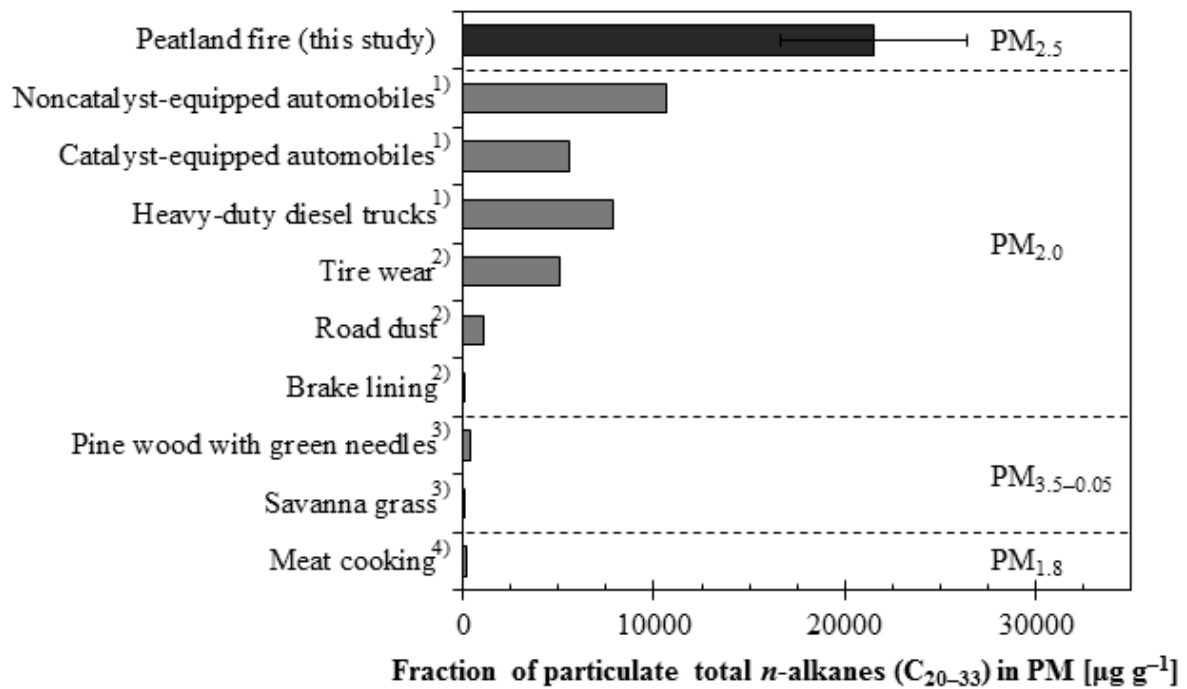
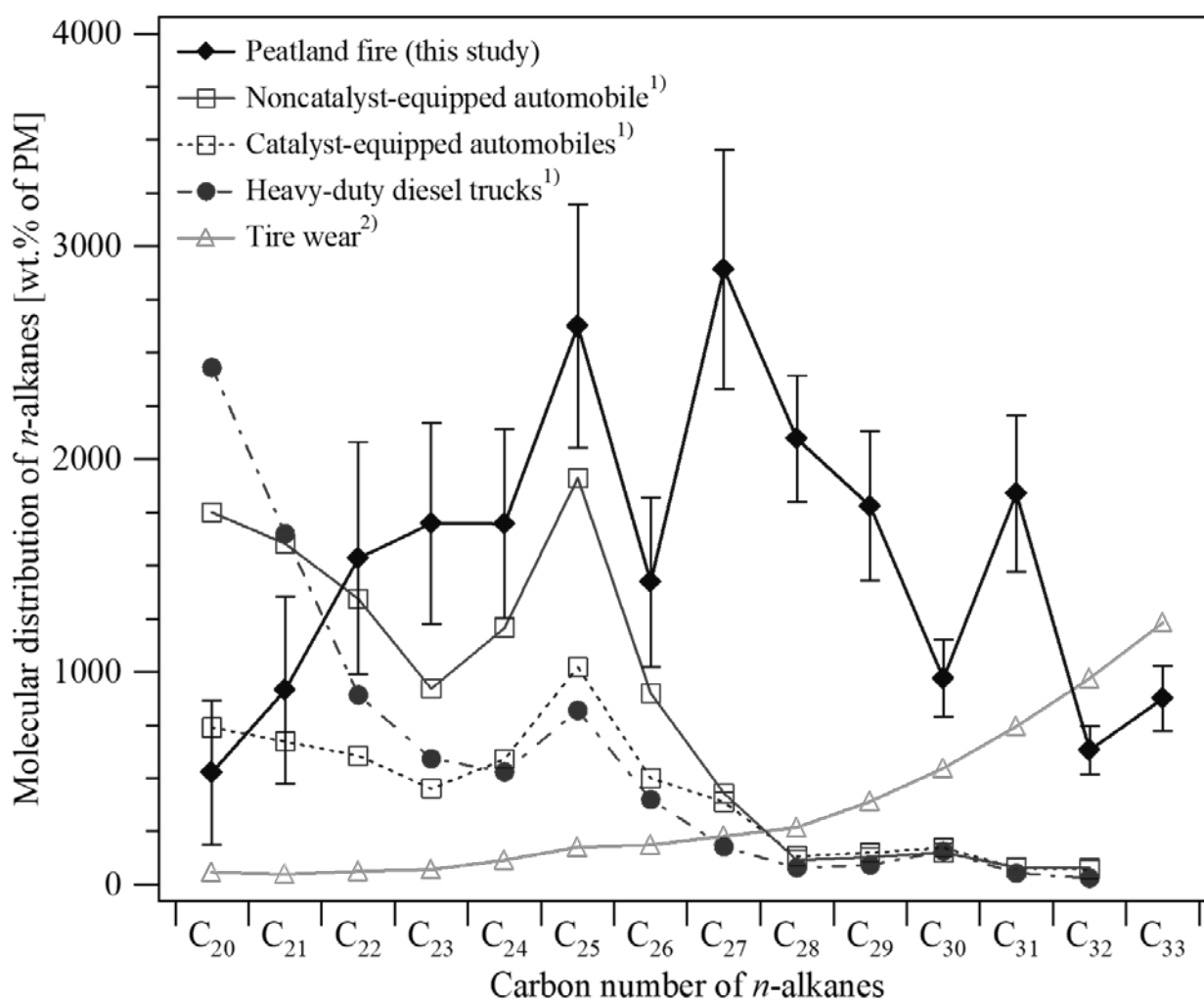


Fig. 2.



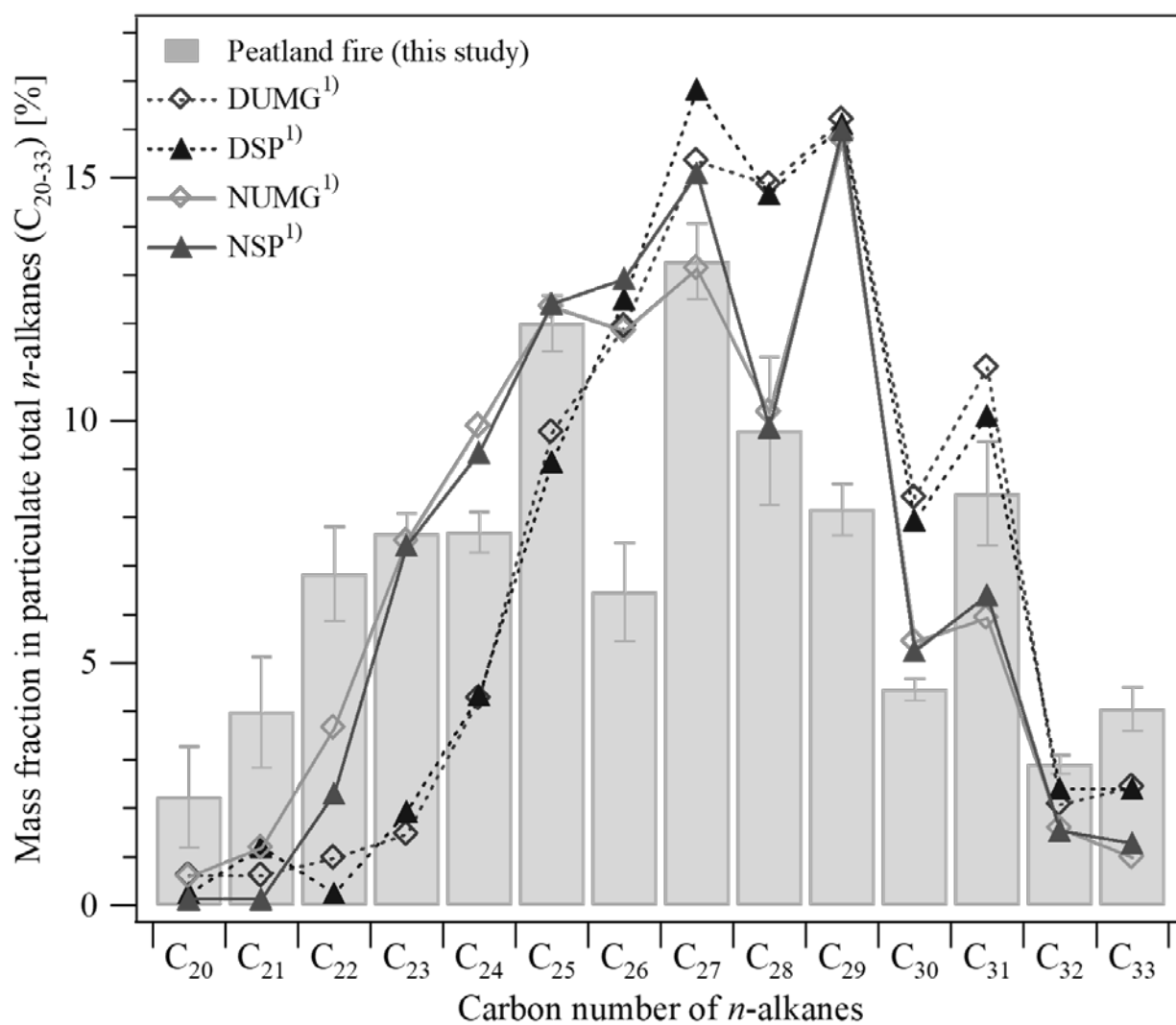
1) data from Rogge *et al.*, 1993a, 2) data from Rogge *et al.*, 1993b, 3) data from Iinuma *et al.*, 2007, 4) data from Schauer *et al.*, 1999.

Fig. 3.



1) data from Rogge *et al.*, 1993a, 2) data from Rogge *et al.*, 1993b.

Fig. 4.



1) data from Abas *et al.*, 2004.

Fig. 5.